Studies of Sub-Micron Phase Segregation in Polyurethane Polymers by Soft X-Ray Spectromicroscopy

Adam P. Hitchcock[1], Tolek Tyliszczak[1], John Brash[1, 2], Rena Cornelious[2], Yew-Meng Heng[2], Stephen G. Urquhart[1,3], Adrian Garcia[3,6], Harald Ade[3], Edward G. Rightor[4,5], Werner Lidy[4], Gary E. Mitchell[5], Rick Steele[6], George Meigs[6] and Tony Warwick[6]

1. BIMR, McMaster University, Hamilton, ON L8S 4M1, Canada
2. Pathology, McMaster University, Hamilton, ON L8S 4M1, Canada
3. Dept. of Physics, North Carolina State University, Raleigh, NC 27895
4. Dow Chemical, B-1470, 2301 N. Brazosport Blvd. Freeport, TX 77541
5. Dow Chemical, 1897 Building, Midland, MI 48667
6. Advanced Light Source, Lawrence Berkeley Lab, Berkeley, CA 94720

INTRODUCTION

The morphology and chemistry of segregated phases determines the physical and chemical properties of many complex polymers, including polyurethanes. Achieving a better understanding of the connections between formulation chemistry, the chemistry and morphology of segregated phases, and the physical properties of the resulting polymer, has the potential to rationalize the development of improved polyurethane-based materials for many applications, ranging from the pedestrian (diapers) to the profound (blood contact polymers). Near edge X-ray absorption spectroscopy (NEXAFS) carried out with sub micron spatial resolution provides imaging and quantitative chemical analysis (speciation) of individual segregated phases.[1,2] We are using the beam line 7.0.1 zone plate microscopes – both the scanning transmission x-ray microscopes (STXM) and the scanning photoemission x-ray microscope (SPEM) - to record images and spectra of model and real polyurethane polymers.

A major thrust over the past year has been to improve the performance of these instruments to take full advantage of the high brightness of the ALS. We are also developing techniques for examining the surfaces (~1 nm) of dry polymers, and for studies of the bulk of fully hydrated polymers (wet cells).[3] Ultimately we hope to develop techniques to examine the *surface* of fully hydrated polymers in contact with blood components (cells, proteins, etc). Here we report on: (i) progress in STXM performance, (ii) application of the UHV SPEM to polymer surfaces, (iii) development of a total electron yield detector for surface studies at atmospheric pressure in STXM, (iv) use of the STXM for quantitative chemical analysis at the C 1s and O 1s edges. Work using a wet cell to study hydrated polymers is described elsewhere.[3]

(i) PERFORMANCE IMPROVEMENTS

In 1997 the standard detector for STXM was changed from gas ionization to a scintillation detector. This has greatly improved the efficiency, dynamic range, and reliability. Identification and elimination of several sources of systematic noise, in conjunction with a major improvement in the scan speed of the fine scale imaging stage, has enabled us to progress from typical dwells of 20 msec/pixel to 0.5 msec/pixel. This has dramatically increased throughput. Working in a different frequency regime has significantly reduced the influence of remaining systematic noise sources on spatial resolution and chemical contrast.

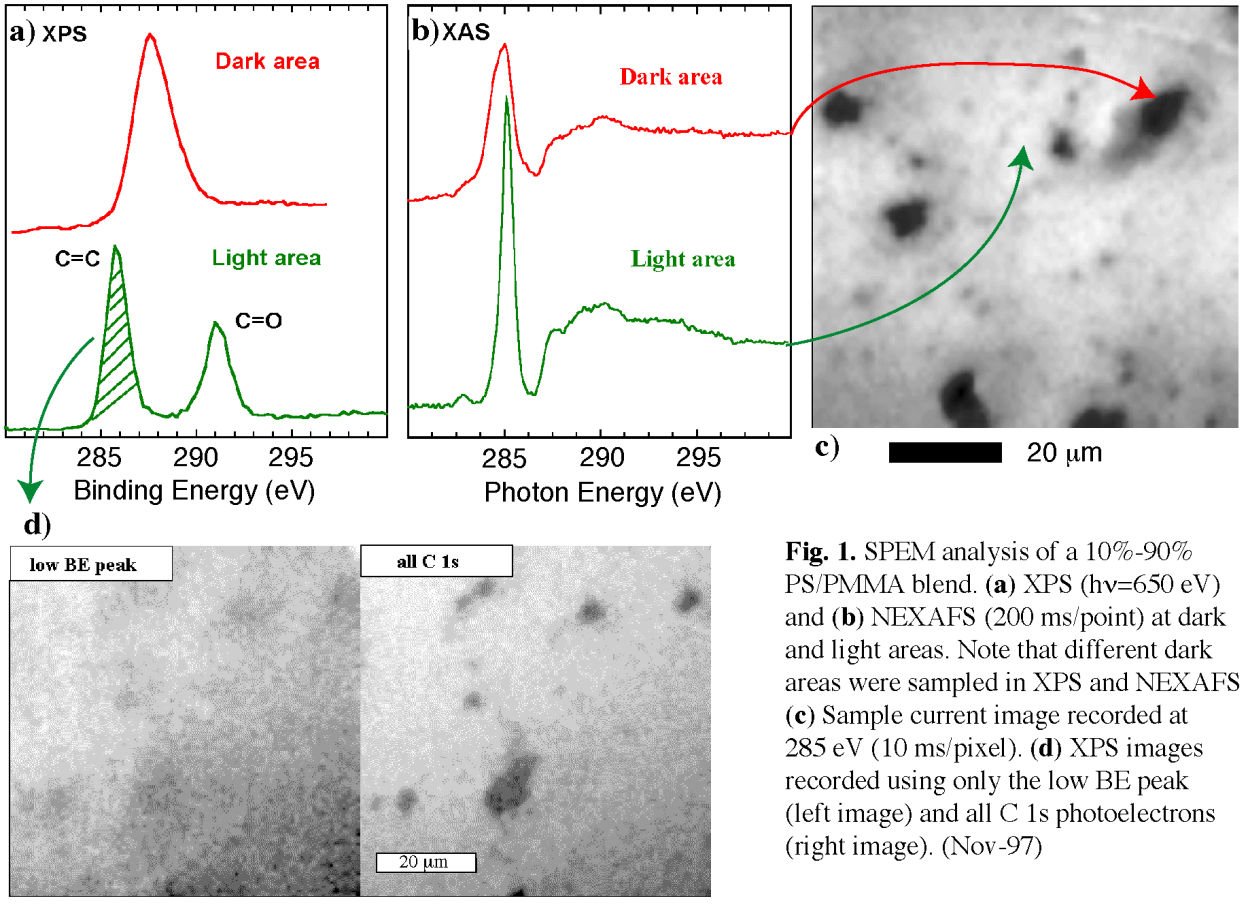

Fig. 1. SPEM analysis of a 10%-90% PS/PMMA blend. (**a**) XPS (hν=650 eV) and (**b**) NEXAFS (200 ms/point) at dark and light areas. Note that different dark areas were sampled in XPS and NEXAFS. (**c**) Sample current image recorded at 285 eV (10 ms/pixel). (**d**) XPS images recorded using only the low BE peak (left image) and all C 1s photoelectrons (right image). (Nov-97)

(ii) SPEM EXPERIMENTS

A 10%polystyrene-90%polymethyl-methacrylate (PS/PMMA) sample was examined by SPEM. C 1s photoemission spectra (nano-XPS) of the PS/PMMA sample clearly distinguished two components (C=C and C=O signals) which were used for selective XPS imaging (**Fig. 1**). Total electron yield (sample current) NEXAFS measurements were also carried out on the PS/PMMA sample. Imaging with 285 eV incident photon energy showed a microstructure similar to that observed in TEM images of samples prepared similarly. The NEXAFS spectrum in the light areas indicates polystyrene is strongly surface segregated, as expected. The XPS and NEXAFS of the dark regions suggest surface contamination rather than PMMA-rich regions. However differential charging effects or radiation damage may also play a role in this image contrast.

(iii) SURFACE IMAGING AT ATMOSPHERIC PRESSURE IN STXM

Fig. 2 presents STXM images and C 1s spectra of a complex model polyurethane (355-PIPA/SAN) in one atmosphere of He, recorded *simultaneously* with transmitted light (I_t) and total electron yield (TEY). The TEY images were recorded using the current to an adjacent electrode ~30 μm away. They exhibit the same microstructure as that seen in the transmission image. In particular they reflect the known chemical composition of the sample - only styrene acrylonitrile (SAN) particles are imaged at 287 eV ($\pi^*_{C/N}$) while both SAN and carbamate (PIPA) particles are imaged at 285 eV ($\pi^*_{C=C}$). This is a clear demonstration that TEY detection in STXM can provide imaging of the near surface region at the limit of STXM spatial resolution. To our knowledge this is the first demonstration of TEY imaging *at atmospheric pressure* at such a low photon energy. Spectra recorded in spot mode with a much longer dwell (~2 s/point) did not exhibit the expected spectral signatures of the SAN and polyurethane matrix. The reason is not yet known, but may be

related either to surface contamination or to charging. We hope to take this detection technology from demonstration to high efficiency and reliability over the next year. If successful, TEY detection will relax sample preparation constraints for 'bulk' investigations (it is difficult to make artifact-free 100 nm thin sections in some materials), and open up the exciting field of surfaces of "real-world" polymers. Simultaneous studies of the surface (~1-5 nm) and bulk (~100-300 nm) of the same material will be extremely valuable for investigations of surface segregation phenomena which are important in many areas, including optimization of biomaterials for blood contact.

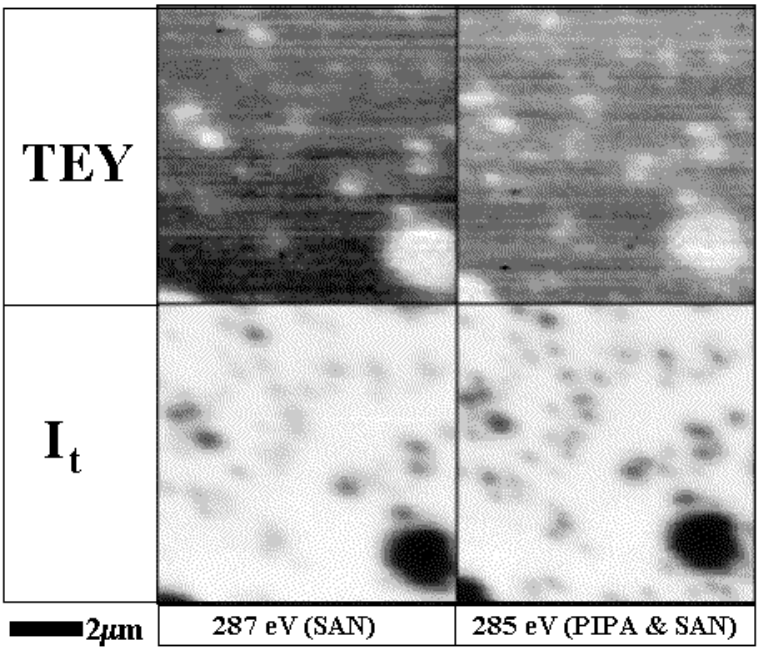

Fig. 2 Images of a polyurethane with two types of filler particles (sample #355) recorded using total electron yield (TEY) and transmitted flux simultaneously in the STXM. The particles seen in both images are SAN whereas those only seen in the right hand images are PIPA. A relatively long dwell (100 ms) and analog filtering were used to obtain adequate quality in the TEY images. The STXM chamber was filled with one atmosphere of He for these measurements.

(iv) QUANTITATIVE ANALYSIS OF POLYURETHANES AT C 1s AND O 1s EDGES

Quantitative chemical analysis can be achieved either by recording images at photon energies corresponding to transitions specific to particular functional groups (*spectro-microscopy*) or by recording core excitation spectra at selected points in the sample (*micro-spectroscopy*). Fig. 2 is an example of the first type. **Fig. 3** is an example of quantitative analysis using spot spectra. The C 1s spectra of two model polyurethanes have been analyzed to determine chemical composition with a few mole % accuracy. In this case normalized spectra, on an oscillator strength per C atom scale, of poly-TDI-urethane (TDI - toluene diisocyanate), poly-TDI-urea, and poly-ether homopolymer models are combined to reproduce the C 1s spectra of the model polyurethanes with different urea/urethane content. The urea/urethane ratio can be determined with reasonable accuracy even when the total (urea + urethane) hard segment component is only 20-30% of the total formula weight.[4]

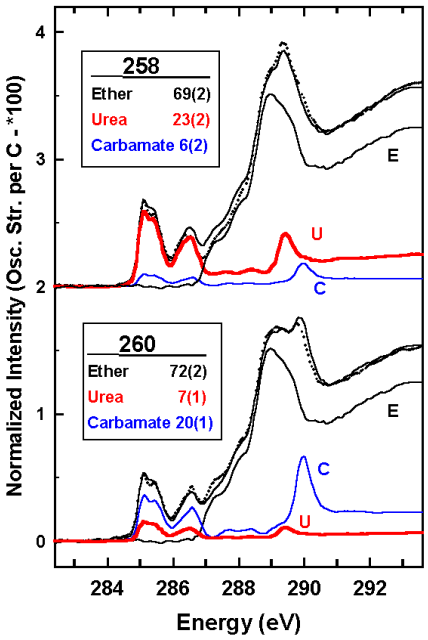

Fig. 3 Compositional analysis of model polyurethanes using sums of C 1s NEXAFS of polymer models. The results agree within 3% of those based on formulation.

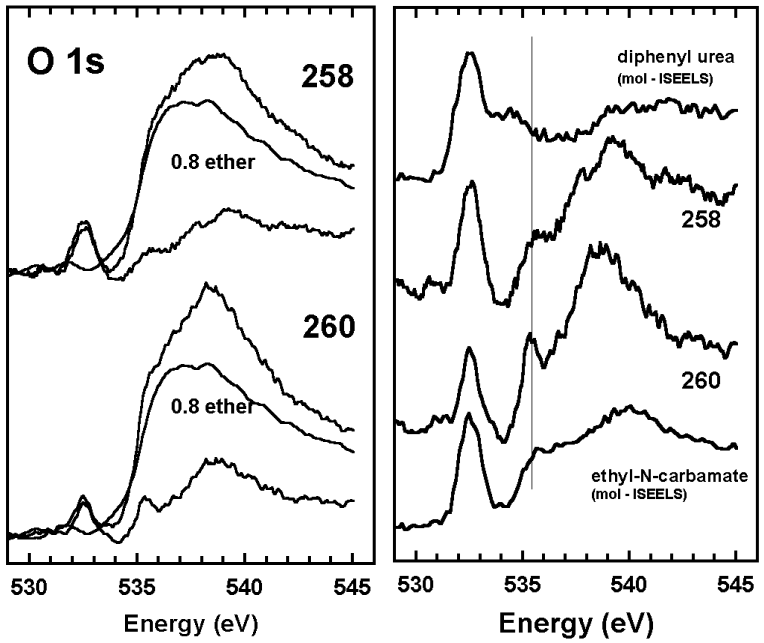

Fig. 4 O 1s spectra of model polyurethanes. *Left*: isolation of aromatic component by subtraction of gaseous ether spectrum. *Right*: comparison of isolated aromatic component with the spectra of gas phase urea and urethane model compounds.

Fig. 4 illustrates the sensitivity to polyurethane chemical composition of O 1s NEXAFS spectra recorded in the STXM. Even though the spectra are dominated by the strong signal from the majority poly-ether component, subtraction of an appropriate model reveals a sensitivity to the aromatic constituents. The changes in the 534-536 eV region indicate one will be able to make a semi-quantitative evaluation of the urea/urethane composition at the O 1s edge. Spectral decomposition procedures like those illustrated in Figs. 3 and 4 are being used to quantify the urea/urethane composition of phase segregated regions in order to study relationships between formulation, processing methodology and properties in a range of polyurethane samples.

ACKNOWLEDGMENTS

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Principal Investigators: **Edward G. Rightor**, Analytical Sciences, Dow Chemical, 1897 Building, Midland, MI 48667 USA. Email: rightor@dow.com. Tel: (409) 238-3616. **Adam P. Hitchcock**, BIMR, McMaster University, Hamilton, ON L8S 4M1 Canada. Email: aph@mcmaster.ca. Tel: (905) 425-9140 ext. 24749.